

Silica scale control by non-ionic polymers: The influence of water system impurities

Z. Amjad

School of Arts and Sciences, Walsh University, N. Canton, Ohio, 44720, USA

E-mail: zamjad@walsh.edu

Abstract

Silica and metal silicate are perhaps the most undesirable deposit encountered in industrial water systems including cooling, desalination, and geothermal. Conventional anionic scale and deposit control agents are not effective in controlling silica-based scales. The complexity of controlling silica laden waters stem from the limited solubility of both amorphous (polymerized) silica and metal silicates. Once formed, silica scale is extremely difficult to remove and often requires the use of mechanical and/or chemical methods. Several laboratory evaluations were conducted to better understand the performance of non-ionic polymers as silica polymerization inhibitors. The impact of system impurities such as trivalent metal ions (Al^{3+} , Fe^{3+}) and suspended matter (clay) on the performance of silica inhibitors was also evaluated.

Key words: *silica, scaling, polymerization, inhibition, non-ionic polymers, trivalent metal ions, suspended matter.*

Received: January 17, 2016. Published: March 12, 2016.

doi: [10.17675/2305-6894-2016-5-2-1](https://doi.org/10.17675/2305-6894-2016-5-2-1)

1. Introduction

Silica (SiO_2) exists in many crystalline and amorphous forms. Crystalline silica has a very low solubility in water, on the order of 6 mg/L SiO_2 . By contrast, amorphous silica has a much higher solubility in the range of 100 to 140 mg/L SiO_2 . The potential for silica scaling increases when the dissolved silica level in an aqueous system exceeds the amorphous silica solubility. When dissolved in water, silica forms silicic acid $\text{H}_4\text{Si}(\text{OH})_4$. However, at silica concentration above 140 mg/L, silicic acid undergoes base-catalyzed polymerization leading to the formation and deposition of colloidal polysilicic acid on heat exchanger and reverse osmosis (RO) membrane surfaces. Silica scaling of heat exchangers and RO membranes can occur by one of the three possible routes: (a) condensation of monomeric silicic acid on solid substrates containing “–OH” group, (b) polymerized silicic acid or colloidal silica deposition, and (c) biogenic amorphous silica by living organisms.

Providing cost-effective solutions for reducing fouling of equipment surfaces by silica and metal silicate salts in industrial water systems using silica laden feed waters continues to challenge water technologists. In evaporative cooling systems, water technologists must maintain silica at acceptable levels (usually below 180 mg/L in the absence of silica and

metal silicate control agents) to avoid silica-based deposits. This requires operating systems at low cycles of concentration resulting in consumption of large amounts of water (which increases water cost) and/or incorporation of silica/silicate control agents in the water treatment formulations. In RO systems silica-based fouling problems cause permeate quality, and more frequent membrane cleaning. In geothermal applications, factors such as variable fluid compositions, fluctuating plant operating conditions, and the complex nature of silica polymerizations collectively make silica scale control a challenging problem.

Another type of silica deposit commonly encountered in RO systems is magnesium silicate. The precipitation of magnesium silicate strongly depends on solution pH and temperature. In RO systems operating above pH 9, magnesium silicate is very likely to form due to the presence of magnesium hydroxide and silicate ions. Although other hydroxide salts such as calcium, strontium, and sodium can react with silicate ions, but resulting products are much more soluble and hence less likely to foul the membrane [1]. The use of polymeric dispersant to control silica/silicate in RO system has been reported [2]. The results of a pilot RO study showed that deposition of silica and magnesium silicate on membrane surface can be prevented by the use of a polymeric dispersant. Further, based on three pilot studies, the following guidelines were proposed for using a polymeric dispersant for silica control [2]:

1. Maintain silica below 240 mg/L as SiO₂;
2. For pH < 7.5: Maintain Mg × Si < 220,000;
For pH > 7.5: Maintain Mg × Si < 110,000
(where Mg is expressed as CaCO₃, Si expressed as SiO₂);
3. Iron and aluminum levels must not exceed 0.05 mg/L in the feed water.

Another investigator discovered that, if all multivalent cations are removed from the feed water stream and the RO system is operated at high pH (pH 10 to 11), silica concentrations of up to 450 mg/L can be tolerated without the use of dispersants or inhibitors [3]. However, this technique is limited to systems that can be successfully operated at pH > 10.

The problem of silica scaling is exacerbated in presence of low levels of polyvalent metal ions (*i.e.*, aluminum, iron, calcium, magnesium, *etc.*) [2]. In addition, corroded steel pipes and heat exchangers are very prone to silica scaling. The composition and quantity of silica scale as well as the rate at which it forms is dependent on pH, temperature, the ratio of calcium to magnesium, and the concentration of polyvalent metal ions [3]. Furthermore, silica deposits are particularly difficult to remove once they form necessitating the use of strong chemical cleaners (based on hydrofluoric acid) or laborious mechanical removal methods.

Neofotistou and Demadis [4] investigated the performance of several polyaminoamide-based dendrimers as silica inhibitors for cooling water applications and observed that inhibitor performance strongly depends on the branching present in the dendrimer. The performance of a formulated product containing hydroxyl phosphono

acetic acid and a copolymer of acrylic acid:allylhydroxy sulfonate ether in high hardness waters containing high alkalinity and 225 mg/L silica has been reported. The inspection of the heat exchangers showed essentially no deposits in the presence of formulated product compared to heavy silica and silicate scale deposits in the control (no treatment) [5].

Amjad and Yorke [6] in their evaluation of polymers reported that cationic-based copolymers are effective silica polymerization inhibitors. Similar conclusions were also reached by Harrar *et al.* [7] when investigating the use of cationic polymers and surfactants in inhibiting silica polymerization under geothermal conditions. Although these cationic-based homo and copolymers showed excellent silica polymerization inhibition performance, they offered poor silica/silicate dispersancy activity. Gallup and Barcelon [8] investigated the performance of several organic inhibitors as alternatives to strong acids for geothermal applications. Results of their study reveal that brine acidification always outperformed organic inhibitors.

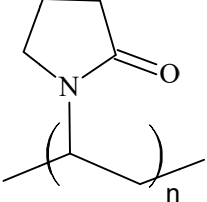
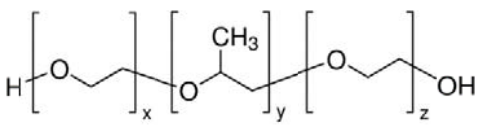
The synergistic effect of polycation and polyanion on silica polymerization was recently investigated [9]. Results of this study reveal that addition of polyepoxy succinic acid (PESA) to silica supersaturated solution containing adipic acid:amine terminated polyether:diethylenetriamine copolymer (polycation) improves the performance of polycation as silica polymerization inhibitor. Recently, Amjad and Zuhl investigated the effect of thermal stress on the performance of a proprietary polymers. It was shown that polymer performance as silica polymerization is affected by thermal stress (temperature, exposure time, polymer concentration, *etc.*) [10].

Among the various dissolved impurities present in the natural waters, metal ions including aluminum, copper, iron, manganese, and zinc when present at low concentrations *e.g.*, few mg/L, pose the most serious problems in many domestic and industrial applications. These metal ions will not only form insoluble hydroxides under acid and/or alkaline pH conditions and deposit on equipment surfaces but will also influence the performance of scale inhibitors and dispersants commonly used in water treatment formulations [11, 12]. Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies but are also toxic to many life forms [13]. Industrial processes such as paint manufacturing, printed circuit board manufacturing, metal polishing, and wood preservatives generate wastewater containing heavy metal contaminants. Because most heavy metals are non-degradable into nontoxic end products, their concentrations must be reduced to acceptable levels before discharging them into environment. Otherwise, these could pose threats to public health and/or affect the aesthetic quality of potable water. Over the years, various methods have been developed to remove toxic metals from aqueous streams. These approaches include precipitation, ion exchange, coagulation, adsorption, and membrane-based filtration processes.

Iron and aluminum fouling often occurs in cooling water and desalination processes as a result of carryover from clarifiers, where iron- and aluminum-based salts are used as coagulants or where raw water (*i.e.*, well water) may be high in iron. Iron levels up to

2 mg/L or greater in the circulating water can be controlled by incorporating dispersant into the water treatment formulation. In cooling water iron oxide (Fe_2O_3 , hematite) and FeOOH are the two most common iron deposits. Magnetite (Fe_3O_4) is rarely encountered in cooling systems. Magnetite needs high temperatures and anaerobic conditions. In our recent investigations it was shown that both soluble and insoluble impurities present in feed water exhibit strong antagonistic effect of the performance of inhibitors used to control various scales such as calcium carbonate, calcium sulfate, and calcium phosphate [14, 15, 16]. In the present work, the impact of soluble impurities (*e.g.*, Al, Fe) and insoluble impurities (*e.g.*, clay, iron oxide) on the performance of two non-ionic polymers, namely, poly(2-ethyl-2-oxazoline), poly(vinyl pyrrolidone), polyethylene polypropylene block copolymer and propylene glycol as silica polymerization inhibitors. Table 1 shows the composition, functional groups, molecular weight (MW) and acronyms for the polymers used. All additives tested were commercial materials.

Table 1. Additives tested.

Additive	Structure	Molecular Weight	Acronym
Poly(2-ethyl-2-oxazoline)	$\begin{array}{c} \text{---}(\text{N} - \text{CH}_2 - \text{CH}_2)_n\text{---} \\ \\ \text{CO} \\ \\ \text{CH}_2\text{CH}_3 \end{array}$	5,000	PEOX
Poly(vinylpyrrolidone)		30,000	PVP
Ethylene oxide propylene oxide block copolymer		8,400	PL68
Propylene glycol	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{OH} \\ \\ \text{OH} \end{array}$	79	PGL

2. Experimental

2.1 Materials

Grade A glassware and analytical grade chemicals were used. Silicate stock solutions were prepared from sodium metal silicate, filtered through 0.2 μm membrane filter, and filtrate analyzed spectrophotometrically using molybdate method [17]. Standard solutions of Al(III) and Fe(III) were obtained from Hach Company. Sodium chloride was obtained from Fisher Scientific Company. Poly(2-ethyl-2-oxazoline), poly(vinyl pyrrolidone),

polyethylene polypropylene block copolymer, and propylene glycol used were commercial materials and their stock solutions were prepared on active solids basis. Stock solutions of all chemicals were stored in polyethylene bottles. In-house, nanopure water was used for all experiments. This water was tested for soluble silica and was found to contain negligible amounts.

2.2 Silica polymerization protocol

Silica polymerization experiments were performed in polyethylene containers placed in a double-walled glass cell maintained at 40°C. Silica supersaturated solutions were prepared by adding a known volume of sodium silicate (expressed as SiO₂), sodium chloride, inhibitor, and water in a polyethylene container. After allowing the temperature to equilibrate, the silicate solution was quickly adjusted to pH 7.0 using hydrochloric acid. The pH of the solution was monitored using Brinkmann pH meter equipped with a combination electrode. The pH electrode was calibrated before each experiment with standard buffers.

The progress of silica polymerization reaction was monitored by taking aliquots of silica supersaturated solutions and analyzing the filtrate (0.22 μm membrane filter) spectrophotometrically [12]. The efficacy of the polymer as silica polymerization inhibitor was calculated using the following equation:

$$\text{Percent Silica Polymerization Inhibition (\%I)} = \frac{[(\text{SiO}_2)_p - (\text{SiO}_2)_a]}{[(\text{SiO}_2)_i - (\text{SiO}_2)_a]} \times 100, \quad (4)$$

where the terms above are as follows:

%I = percent silica polymerization inhibition;

(SiO₂)_i = silica concentration at the beginning of experiment;

(SiO₂)_p = silica concentration in the presence of polymer at 20 hr;

(SiO₂)_a = silica concentration in the absence of polymer at 20 hr.

3. Results and Discussion

The use of polymeric additives as components of water treatment formulations has increased significantly in the last two decades. The role of additives in these formulations is fourfold: *a*) to inhibit scale formation, *b*) to disperse particulate matter, *c*) stabilize divalent and trivalent metal ions *i.e.*, Cu, Zn, Mn, Fe, *etc.*, and *d*) to modify crystal structure. Most of the additives that have demonstrated any efficacy in controlling mineral scale are homopolymers containing anionic carboxyl group –COOH (*i.e.*, polyacrylic acid, polymaleic acid, polyitaconic acid, and polyaspartic acid. These homopolymers with molecular weight, MW < 10,000 Daltons have shown to exhibit good to excellent performance in preventing precipitation of various scale forming salts including carbonate, fluorides, and sulfate salts of alkaline earth metals [18, 19, 20]. On the other hand, acrylic acid and maleic acid copolymers containing various functional groups, *i.e.*, –COOR, –SO₃H, CONR₁R₂, *etc.*), have shown good to excellent performance as calcium phosphate and calcium phosphonate scale inhibitors, and dispersants for suspended matter (*i.e.*, clay,

iron oxide) but poor to mediocre performance for carbonate and sulfate based scales [18, 19, 20]. In our previous investigation, polymers from both these categories were shown to exhibit poor performance as silica polymerization inhibitors thus suggesting that anionic functional group show poor interactions with the silanol ($-\text{Si}-\text{OH}$) group present in silicic acid.

3.1 Performance of non-ionic polymers: To evaluate the performance of homopolymers containing non-ionic groups, silica polymerization inhibition experiments were carried out in the presence of varying concentration of PEOX and as a function of time. The conditions employed were: 650 mg/L silica as SiO_2 , pH 7.0, 40°C , using the testing protocol described previously [17]. Figure 1 shows profile of soluble SiO_2 as a function of time. There are three points worth noting: *a)* silica polymerization occurs immediately with <1 min induction time, *b)* soluble silica concentration decreases with increasing reaction time, and *c)* soluble silica concentration depends on the inhibitor concentration. For example, soluble silica concentrations obtained at 20 h in the presence of 10 and 25 ppm of PEOX are 252 and 404 mg/L respectively, compared to 178 mg/L obtained in the presence of 0 ppm of PEOX.

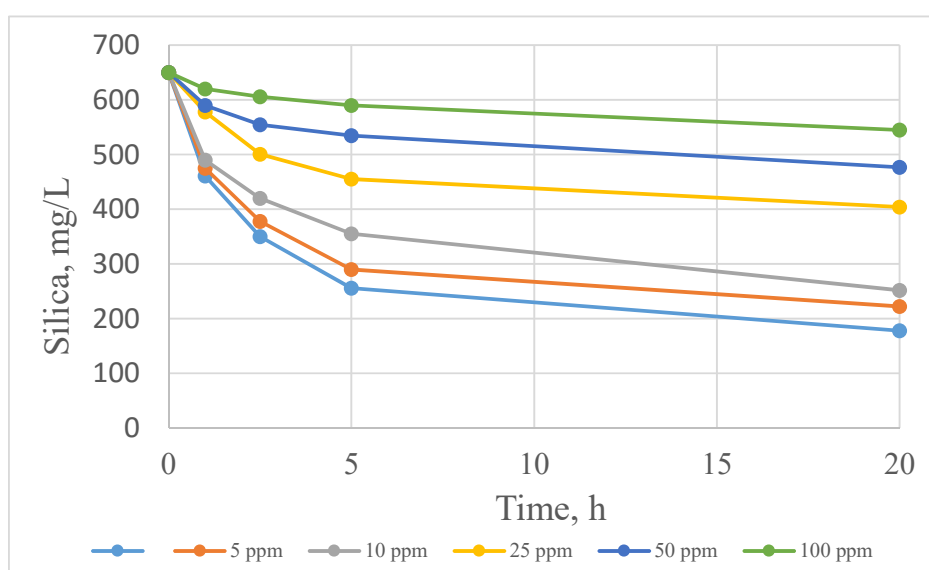


Figure 1. Silica polymerization in the presence of varying concentration of PEOX and as a function of time.

Figure 2 presents inhibition data, calculated according to equation (1), vs. PEOX dosage profile at 20 h. It is evident that silica inhibition strongly depends on PEOX concentration. For example, %*I* value obtained in the presence of 5 ppm is $< 5\%$ compared to 11% obtained in the presence of 10 ppm PEOX. As illustrated increasing the PEOX concentration by a factor of 2.5, (*i.e.*, 10 to 25 ppm) results in almost five fold (from 10 to 53%) increase in % inhibition value.

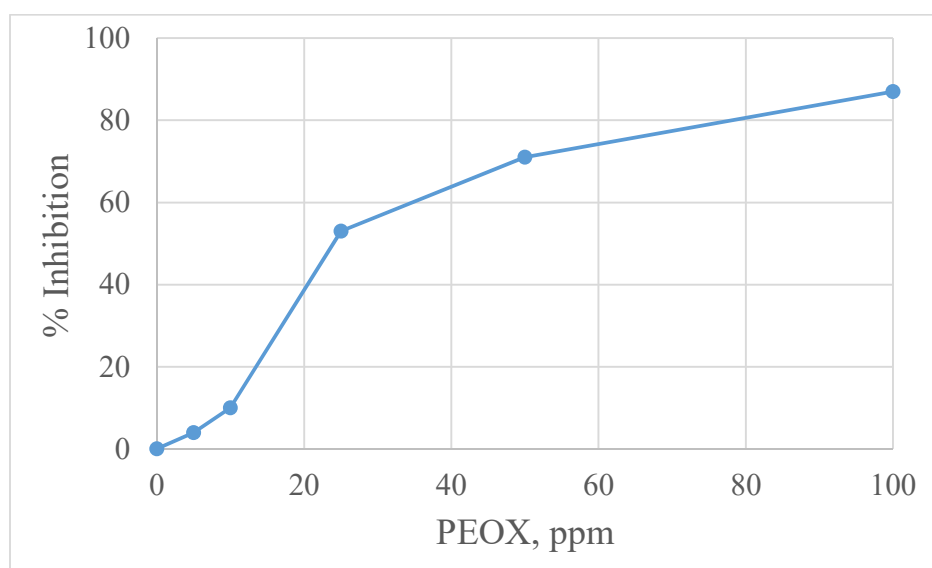


Figure 2. Plot of silica inhibition as a function of PEOX, 20 h.

To investigate the efficacy of additives containing non-ionic functional groups, a series of silica polymerization experiments were conducted under similar experimental conditions. Results collected at 20 h and in the presence of 50 ppm of various additives are depicted in Figure 3. It is evident that additive performance as silica polymerization inhibitor strongly depends on additive architecture with PGL (propylene glycol), a non-polymeric additive, shows the poor performance (<10 %I). Based on the data presented additives can be ranked as follows: PEOX > PL68 > PVP >> PGL.

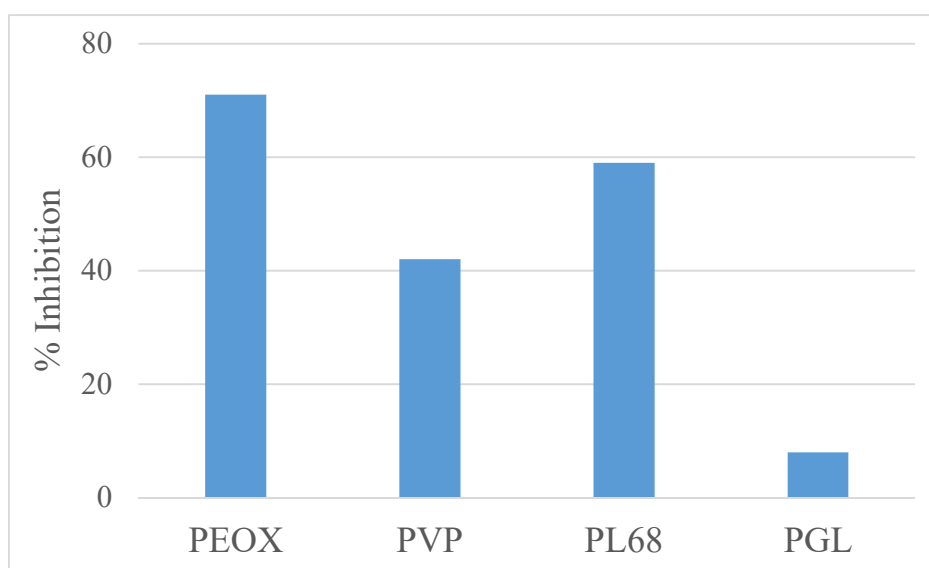


Figure 3. Plots of % silica inhibition at 20 h and in the presence of 50 ppm of various additives.

3.2 Effect of trivalent metal ions: Iron and aluminum based compounds (e.g., ferric sulfate, alum, sodium aluminate) have been utilized for decades as coagulant aids to help facilitate municipal and industrial water clarification. These inorganic flocculating agents neutralize the charge of water borne turbidity particles and they hydrolyze to form insoluble hydroxide particles that entrap additional particles. In most cases, these large particles (or flocs) are removed *via* settling in a clarifier and are collected as sludge. Occasionally, clarifier upsets cause these metal-ion containing flocs and/or unused flocculant to carryover or escape pretreatment system and become contaminants or impurities in cooling or boiler feed waters that can affect the performance of the treatment program. Additionally, soluble iron, ferrous ion, is often encountered in natural water systems either from water itself at low concentrations (usually less than 3 mg/L) or as a result of corrosion of iron piping, well heads, or other vessels in the system. On oxidation, the ferric ions (Fe(III) or Fe^{3+}) may form soluble and/or insoluble complexes with hydroxide and/or inhibitors, thus reducing effective concentration of inhibitor in calcium phosphate supersaturated solution.

To understand the impact of trace levels of Al(III) or Al^{3+} , several silica polymerization experiments were carried out in the presence of 50 ppm of inhibitors and varying dosages of Al^{3+} . Results presented in Figure 4 clearly show that low levels (*i.e.*, 0.15 mg/L) of Al^{3+} exhibit an antagonistic effect of the performance of PEOX, PVP, and PL68. As shown in Figure 4, further increase in Al^{3+} concentration from 0.15 to 0.25 mg/L results in further decrease in %I values of all the three inhibitors. Based on the data presented, the percent loss in inhibitor performance observed in the presence of 0.15 mg/L is ~20% compared to ~50–60% loss in the presence of 0.25 mg/L Al^{3+} .

Figure 4 also presents performance data on the three effective silica polymerization inhibitors, namely, PEOX, PVP, and PL68. As shown in Figure 4, Fe^{3+} ions like Al^{3+} also exhibit negative impact on the performance of silica polymerization inhibitors. In general, the % loss observed at 0.25 mg/L Fe^{3+} is ~25% compared >50% loss observed in the presence of 1.0 mg/L Fe^{3+} . It is evident from Figure 4 that under similar experimental conditions, presence of Al^{3+} exhibits more negative impact on inhibitors performance than Fe^{3+} . The observed increase in performance loss with Al^{3+} vs. Fe^{3+} may be attributed to a higher charge density for Al^{3+} . It is worth noting that similar performance trend as observed in the presence study for the impact of trivalent ions has been reported for other scaling systems [24, 25].

To overcome the performance loss observed in the presence of 1.0 mg/L of Fe^{3+} , additional experiments were carried out in the presence of increasing concentration of PEOX. Results depicted in Figure 5 reveal that %I value increases with increasing PEOX concentration. It is interesting to note that it took almost twice the PEOX concentration (from 50 to 100 mg/L) in the presence of 1.0 mg/L Fe^{3+} , to achieve similar performance as obtained in the presence of 50 ppm of PEOX and 0 mg/L of Fe^{3+} .

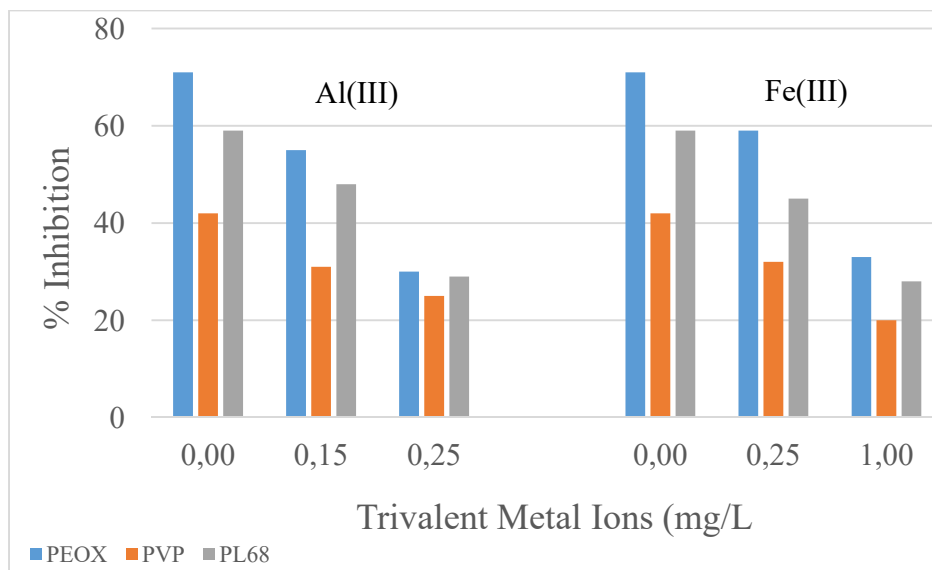


Figure 4. Effect of different concentration of trivalent ions in the presence of 50 ppm of additives.

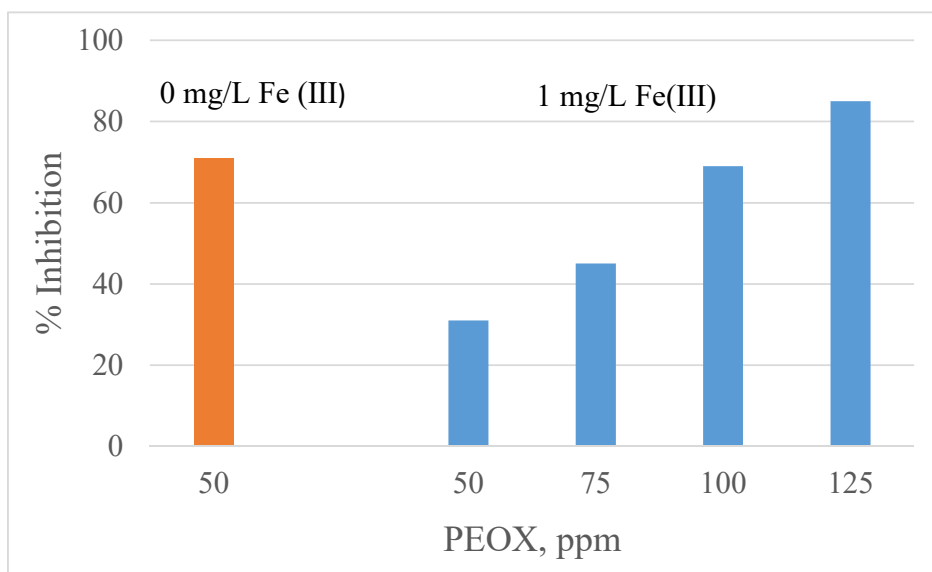


Figure 5. Effect of varying concentration of PEOX in the presence of 1 mg/L Fe(III).

3.3 Effect of suspended solid: Suspended solids such as clay, corrosion products, algae, bacteria, and metal carbonates, are commonly encountered substances in feed and/or recirculating waters that are not completely soluble and are present as particles. These suspended solids not only lead to high turbidity but also provide a large surface area for adsorption of dissolved chemical species. The solids concentration usually ranges from <math><5\text{ mg/L}</math> to $>200\text{ mg/L}$, but can go up to $>50,000\text{ mg/L}$ during flood [26]. Particles of a size above 200 nm usually impart a visible turbidity to waters. With the increasing shortage of good quality feed water, environment constraint, and the systems operating under stressed conditions, the fouling of heat exchanger and RO membrane surfaces, and

clogging of pipes by suspended solids, is becoming a major concern for the efficient operation of such industrial systems. Since the complete removal of suspended solids from process waters is not a feasible approach if large volumes are used, dispersants are normally incorporated in the water treatment formulations to stabilize and/or disperse suspended solids.

Additives commonly used in water formulation generally fall into two categories namely polymeric (*i.e.*, PAA, PMA, PIA, and copolymers containing different functional groups) and non-polymeric (*i.e.*, polyphosphates, phosphonates, *etc.*). Additives from both these types are known to adsorb onto particles that may be present in water. The adsorption of additives onto particles and the resultant interactions between particles is the mechanism of dispersion. However, when an additive is consumed in dispersing particles, it is not available to inhibit the formation of scale forming salts. In addition, suspended particles could act as nuclei for the formation of mineral scales. The magnitude of the impact of suspended matter such as clay was tested by running several silica polymerization experiments in the presence of 100 mg of clay and 50 ppm of silica inhibitors. Results presented in Figure 6 clearly show that addition of clay particles to silica supersaturated solution exhibits an antagonistic effect on silica polymerization inhibitors. For example, % loss in performance of PEOX, PVP, and PL68 is ~50%. It is worth noting the antagonistic effect as shown by clay particles in the present study has been reported for other scaling systems [26, 27].

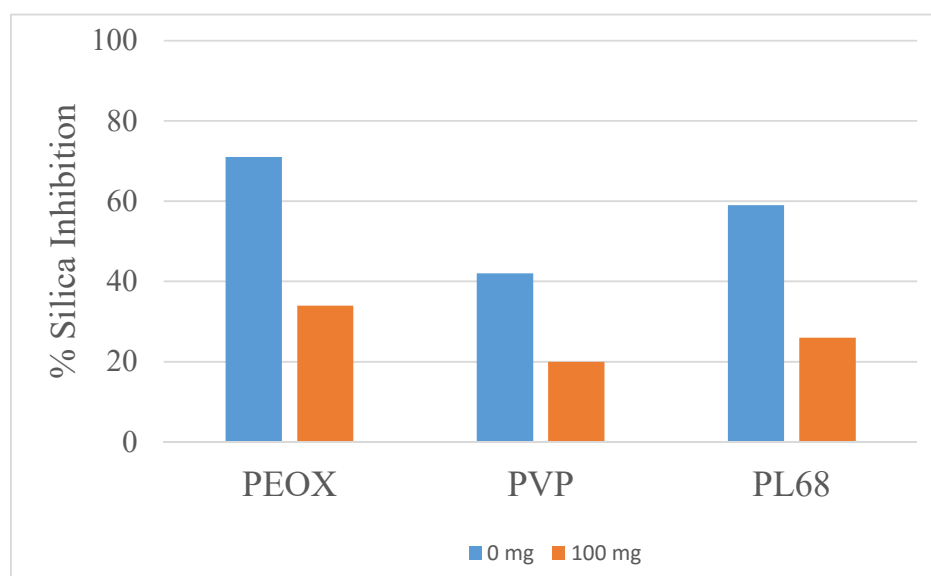


Figure 6. Plots of % silica inhibition in the presence of 50 ppm of additives and 100 mg of clay.

Summary

The potential for silica scaling occurs when the dissolved silica in re-circulating water or reject stream in RO system exceeds the solubility limit at ambient temperature for amorphous silica. To avoid the formation of silica-based deposits, which are very difficult to remove safely and economically, water technologists typically employ conservative operating criteria; e.g., cooling system limit cycles of concentration and desalination systems limit recovery. These approaches result in either large water consumption (which increases water costs) and/or water treatment chemical program modification to incorporate silica/silicate control agent.

The results presented in this paper show that non-ionic polymers such as poly(2-ethyl-2-oxazoline), poly(vinyl pyrrolidone), ethylene oxide-propylene oxide block copolymer show mediocre to excellent performance as silica polymerization inhibitors. Additionally, results also reveal that both soluble and insoluble impurities exhibit negative impact of varying degree on the performance of silica polymerization inhibitor.

Acknowledgement

The author thanks Walsh University for support to carry out this study.

References

1. C.W. Smith, *Ind. Water Treat.*, 1993, **4**, July/August, 20.
2. P.F. Weng, *Silica scale inhibition and colloidal silica dispersions for reverse osmosis systems*, American Desalting Association, Biannual Meeting, Palm Beach, FL, September 1994.
3. D. McBride and D. Mukhopadhyay, *450 ppm silica sustained in innovative reverse osmosis technology*, International Water Conference, IWC-96-16, Pittsburgh, PA, 1986.
4. E. Neofotisou and K. Demadis, *Desalination*, 2004, **167**, 257.
5. L.A. Perez, J.M. Brown and K.T. Nguyen, *Method for controlling silica and water soluble silicate deposition*, US Patent No. 5,256,302, 1983.
6. Z. Amjad and M. Yorke, *Carboxylic functional polyampholytes as silica polymerization retardants and dispersants*, US Patent No. 4,510,059, 1985.
7. J.E. Harrar, L.E. Lorensen and F.E. Locke, *Method for inhibiting silica precipitation and scaling in geothermal flow systems*, US Patent No. 4,328,106, 1982.
8. D.L. Gallup and E. Barcelon, *Geothermics*, 2005, **34**, 756.
9. B. Zhang, S. Xin, Y. Chen and F. Li, *J. Colloid Interface Sci.*, 2012, **368**, 180.
10. Z. Amjad and R. Zuhl, *Effects of thermal stress on silica-silicate deposit control agent performance*, Association of Water Technologies Annual Convention, Reno, NV, 2010.
11. Z. Amjad, J. Pugh, J. Zibrida and R. Zuhl, *Mater. Perform.*, 1997, **36**, no. 1, 32.
12. Z. Amjad and R.W. Zuhl, *The Influence of water systems impurities on the performance of deposit control polymers as particulate dispersants*, Paper presented at the 2001 Annual Convention of Association of Water Technologies, Dallas, TX, 2001.

13. S.E. Ghazi, A.E. El-Asmy and A.M. Nokrashy, *Indian J. Sci. Technol.*, 2008, **1**, no. 6, 1.
14. Z. Amjad and R. Zuhl, *Kinetic and morphological investigation on the precipitation of calcium carbonate in the presence of inhibitors*, CORROSION/2006, paper no. 06385, NACE International, Houston, TX, 2006.
15. Z. Amjad, *Desalination Water Treatment*, 2011, **36**, 270.
16. Z. Amjad and R. Zuhl, *Phos. Res. Bull.*, 2002, **13**, 59.
17. Z. Amjad, *Int. J. Corros. Scale Inhib.*, 2016, **5**, no. 1, 1.
18. Z. Amjad, *Tenside Surfactants Detergents*, 1999, **36**, 162.
19. Z. Amjad, *Langmuir*, 1993, **9**, no. 2, 597.
20. Z. Amjad, R. Landgraf and J. Penn, *Int. J. Corros. Scale Inhib.*, 2014, **3**, no. 1, 35.
21. Z. Amjad, *Canadian J. Chem.*, 1989, **67**, no. 5, 850.
22. J.A. Wohlever, Z. Amjad and R. Zuhl, *Performance of anionic polymers as precipitation inhibitors for calcium phosphonates*, in *Advances in Crystal Growth Inhibition Technologies*, Kluwer Academic Publishers, New York, NY, 2001.
23. Z. Amjad, *Tenside Surfactants Detergents*, 1999, **36**, 50.
24. C.J. Gabelich, W.R. Chen, T.I. Yun, B.M. Coffey and I.H. Suffet, *Desalination*, 2005, **180**, 307.
25. W.-Yi Shih, J. Gao, A. Rahardianto, J. Glater, Y. Cohen and C.J. Gabelich, *Desalination*, 2006, **196**, 280.
26. B. Bolto and J. Gregory, *Water Res.*, 2007, **41**, 2301.
27. Z. Amjad, *UltraPure Water*, 2011, **27**, no. 3, 32.
28. Z. Amjad, D. Butala and J. Pugh, *The influence of recirculating water impurities on the performance of calcium phosphate inhibiting polymers*, CORROSION/99, paper no. 118, NACE International, Houston, TX, 1999.

